Development of Sustainable Solvent and Its Thermodynamics Study for Polyolefin Polymer Recycling

by

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved by,

_____
(Dr. ABRAR INAYAT)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MOHAMAD HAZWAN BIN ZAKARIA

ABSTRACT

This project is comprised of development of a sustainable solvent for polymer recycling process. The type of polymer used is waste polymer polyolefin. The procedure that is incorporated for recycling these polymers is called dissolution/ reprecipitation method. This procedure required dissolution of polyolefin in solvent and another non-solvent to reprecipitate the solvent. Solvent use in this study is a mixture of toluene and naphthalene at a certain ratio. Results showed that by using this solvent mixture, it can dissolve more polyolefin polymer at a low temperature. For Low Density Polyethylene (LDPE) and High Density Polyethylene (LDPE), the ratio of waste polymer to solvent is 1:20. For Polypropylene (PP), the ratio of waste polymer to solvent is 1:21. All polymers dissolve at temperature of 90 °C.

ACKNOWLEDGEMENT

Praise to the God Almighty for eternal blessing, I finally completed the final dissertation of Final Year Project within time. I would like to express my heartfelt gratitude towards my project supervisor, Dr. Iqbal Ahmed; for his guidance and assistance throughout the project timeline. His support and supervision helped me to complete the project smoothly. Not to mention Dr. Abrar Inayat, who guided me through my second half of the semester in completing my final year project. Next, I would like to thank laboratory personnel for their assist and co-operation that help me to run the experiment. Finally, I would like to thank my parents for their continuous support and encouragement which driven me to complete this project.

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CHAPTER 1 INTRODUCTION

1.1 BACKGROUND STUDY

It would be difficult to view modern society today without polymer. Polymer has found a vast uses in fields as packaging, construction, household appliances, automotive, electronics, medicine, and aerospace component. As can be seen from the list, polymer technology can be applied with great success in a variety of ways. Currently, the world consumed one trillion tons per year of plastic product (Goodship, 2007). As for the average Malaysian, the plastic bag is indispensable in the daily routine. Thus, the plastic bag consumption rate is exceptionally high with the average consumption per individual. Experts predict it may takes between 100 and 500 years for the plastic bags to degrade completely and the process emits carbon emissions that contribute to global warming.

It is estimated that Malaysians on average produce 32,000 tons of solid waste annually with polymer plastic bags and products representing 24 per cent of the total waste (Bernama, 2012). Several ways had been invoked by local authority to reduce the polymer usage in Malaysia. In addition, the government has taken numerous efforts to reduce plastic consumption among Malaysian by promoting awareness activities like greening the surrounding and environment friendly lifestyle. Plus in 2011, the government enforced for a no-plastic day campaign for every Saturday for all supermarket in Malaysia (MPMA, 2011).

In Malaysia, recycling is never become a first option as a way to reduce amount of waste polymer. Instead to manage the solid waste product, it is usually been dumped at a specific area called as landfill. The solid waste polymer is left to be decomposed through natural decomposition. However, this method seems meet a dead end as the increasing amount of waste polymer compared to designated landfill. Another approach to decomposed waste polymer is by using an incinerator. Although this method could save the limited landfill area, but the process uses fuel to burn the waste polymer and will emit harmful greenhouse gases which later will hurt the environment.

Other than that there are few methods for polymer recycling mainly mechanical recycling and chemical recycling. In this study, only mechanical recycling is discussed in details as the methodology used is using mechanical recycling. Thus the method used for mechanical recycling is dissolution and reprecipitation method. During this technique, the polymer can be separated and dissolved in a solvent (dissolution), which later is being precipitated using anti-solvent (reprecipitation). In this method, waste polymer is used and been dissolved in a closed vessel at a certain temperature until the entire waste polymer has been dissolved. The solvent is chosen based on the solubility parameter of the selected polymer, where the value must be closed to each other.

Once dissolution method has taken place, the solvent with dissolvent polymer is brought to reprecipitation method. During this method, the solvent is participated with anti-solvent to recover the dissolved waste polymer. Then the waste polymer is dried and analyzed for its chemical and mechanical structure. From previous research that had been done, the amount of solvent used to recover the waste polymer is very high which is not economical if it is applied into industrial scale. Plus, the dissolution temperature used is very high which requires more energy. Some solvent such as toluene, xylene were used as solvent to dissolve waste polyolefin. As result a high recovery is achieved but it requires 100gram of solvent to dissolvent only 1g of waste polymer at a temperature more than 90°C. Later in next chapter, the result of previous research is discussed in details.

Thus a study is made to tackle the problems encountered in previous research. A sustainable solvent is developed so that more waste polymer can be dissolved at the possible lowest temperature. The attempt is to combine two type of solvent at a certain ratio that has close solubility parameter to the polymer used. Later, the sample is taken for further analysis to make comparison between before and recycling process takes place.

1.2 PROBLEM STATEMENT

Currently, the research on solvent needed to recycle polyolefin polymer yield to

i. Ratio of 1:100 of waste polyolefin to solvent as fix procedure. This ratio required high amount of solvent and produce low recovery of plastic.
ii. Waste polyolefin polymer only can be dissolved in specific temperature which is more than 90°C. The solution will vaporize if the temperature is too high, or the plastic will not dissolve if the temperature is too low.
iii. The selection of solvent is limited by the type of polymer used. This is because the selected solvent is chose according to it solubility in the specific solvent.
iv. Stability of polyolefin: As number of carbon increase the dissolution will increase.

Regarding to the problem statement above, a specific research is conducted to develop a sustainable solvent for polyolefin recycling using dissolution and reprecipitation method.

1.3 OBJECTIVE

i. To increase the ratio of waste polyolefin dissolved to solvent used
ii. To determine most suitable lowest temperature for dissolution method.
iii. To determine the suitable combination of solvent for polyolefin polymer recycling

1.4 SCOPE OF STUDY

There are two main techniques to run experiment. The first is dissolution method, which required a combination of two or more solvents for waste polymer to dissolve. It will use waste plastic solid of polyolefin polymer. The next technique is reprecipitation method, where it will use a non-solvent to reprecipitate the polymer. Finally after achieving high recovery of plastic, the used solvent is further studied to investigate its thermodynamic properties.

This project is a continuation or development to the current research on polyolefin polymer recycling. It is a modification to improve the current result which will reduce the amount of solvent used, hence can reduce the cost without demoting any specification of recycled polymer. The project merely focuses on the development of sustainable solvent for polyolefin polymer from plastic waste. From the objective and planned methodology in carrying out this project, it is believed that the period allocated for Final Year Project is sufficient to complete this research.

CHAPTER 2 LITERATURE REVIEW

2.1 POLYOLEFIN POLYMER

Polymer is made up by sequence of chain of repeated subunits, called monomer. Polyolefin is type of polymer consist from olefin which are polyethylene and polypropylene. They are a major type of plastic used throughout the world in such applications as bags, toys, containers, pipes, housewares, industrial wrappings and film, battery cases, automotive parts, electrical components. (Hadi, Najmuldeen, & Ahmed, 2012) In Western Europe alone approximately 21.37 million tons of these three polymers are consumed each year (data of 2003), representing an amount of 56% of the total thermoplastics (Achillas et. al, 2007).

Low Density Polyethylene (LDPE) is the first grade of polyethylene which produced by using high pressure process via free radical polymerization. LDPE, which has recycling number 4, is widely used as manufacturing containers. This is because LDPE is not reactive at room temperature (Papaspyrides, Poulakis, & Varelides, 1994). Because of LDPE has more branching compared to HDPE, LDPE has lower intermolecular forces and tensile strength (Wikipedia, 2014).

High Density Polyethylene (HDPE), which has recycling number 2, is known for its large strength to density ratio. Although the density of HDPE is higher than LDPE, HDPE has less branching, which in results it gives more intermolecular forces and tensile strength than LDPE.

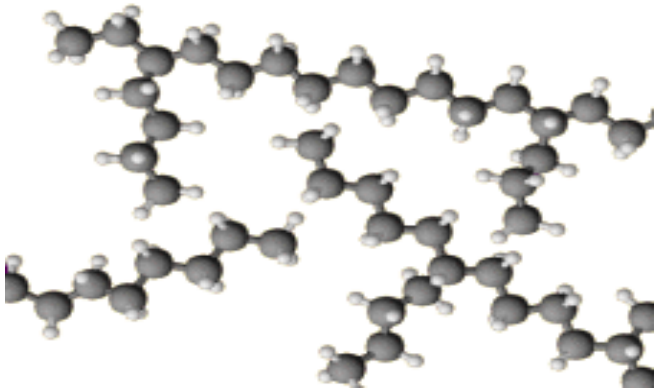


Figure 1: Short Section of LDPE

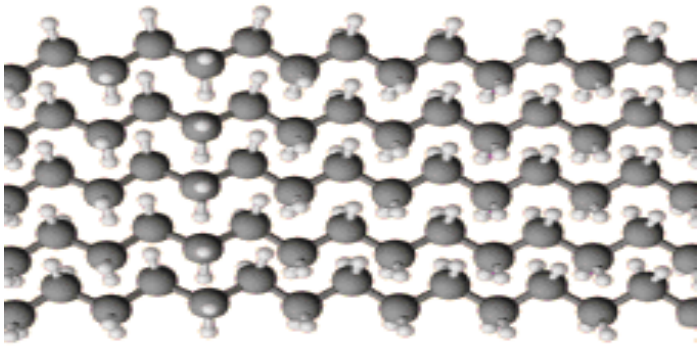


Figure 2: Short Section of HDPE

Polypropylene (PP) was first polymerized in 1954 the German chemist Karl Rehn as well as by the German chemist Karl Rehn to a crystalline polymer (Morres, 2005). Polypropylene, which has recycling number 5, has intermediate level of crystallites between LDPE and HDPE. Polypropylene is reasonably economical, and can be made translucent when uncolored but is not as readily made transparent as polystyrene, acrylic, or certain other plastics.

Figure 3: Short Section of PP

The following is the tabulated properties of polyolefin:

General Properties	**LDPE**	**HDPE**	**PP**
Density	0.92 g/cm^3	0.95 g/cm^3	0.946 g/cm^3
Melting Point	105 to 115 °C	150 to 180 °C	130 to 171 °C
Refractive Index	1.51	1.54	1.49
Limiting Oxygen Index (%)	17	17	18

Table 1: Physical Properties of LDPE, HDPE, PP (Goodfellow, 2014)

Chemical Resistance	LDPE	HDPE	PP
Alcohols	Good	Good	Good
Alkalis	Good	Good	Good
Aromatic hydrocarbons	Fair-Poor	Fair	Fair
Halogenated Hydrocarbons	Fair-Poor	Fair-Poor	Good-Poor
Halogens	Fair-Poor	Fair-Poor	Poor
Ketones	Good-Fair	Good-Fair	Good

Table 2: Chemical Resistance for LPDE, HPDE, PP (Goodfellow, 2014)

2.2 SOLVENT AND SOLUBILITY

Solvent is a substance which is used to dissolve a solute. It can influent reactions in many ways. Purpose of having solvent in a reaction is to have a medium for solute to react easily and as carrier for chemical compound in their solutions to their point of use in the required amounts (Gani, Jiménez-González, & Constable, 2005). Generally, solvent can be categorized into two main sections; polar and non-polar solvent. The dielectric constant usually will determine the polarity of the solvent. Dielectric constant is a measurement that indicates the ability of a solvent to reduce field strength of surrounding electric field when a charged particle is immersed in it. Solvent that having dielectric constant less than 15 is considered to be non-polar solvent (Wikipedia, 2014) (Hansen, 2004).

In this experiment, a good combination of solvent plays an important role determining the success of this project. This is because in mechanical recycling of waste polyolefin polymer, solvent is used to dissolve the waste polymer. Therefore, several parameters of solvent properties needed to be taken into consideration in order to have a good solvent combination. To understand the solvent selection, one must be able to know on the solubility parameter.

Hildebrand solubility parameter is one of the common calculation that being used to actually determine the solubility of a solvent. The fundamental of Hildebrand solubility parameter (δ) is it calculates the degree of interaction between materials numerically. This calculation is proved to be a good solubility indicator especially for non-polar materials such as polymer. This solubility parameter is calculated by Hildebrand by taking the square root of cohesive energy density.

$$\delta = \sqrt{\frac{\Delta Hv - RT}{Vm}} \quad (1)$$

From the equation above, the cohesive energy is simply heat of vaporization divided by molar volume. The cohesive energy density indicates amount of energy needed to detach one unit volume of molecules completely. For a material to dissolve in a solvent, these same interactions need to be overcome as the molecules are separated from each other and surrounded by the solvent. According to the above correlation theory, the solubility parameter for polyolefin is as follows:

Substance	**δ ($cal^{1/2}$ $cm^{-3/2}$)**	**δ ($MPa^{1/2}$)**
Polyethylene	7.9	
Polypropylene	8.2	16.6

Table 3: Hildebrand Solubility Parameter

Referring to from table above, several solvent which has solubility near to polyolefin is tabulated:

Solvent	**δ ($cal^{1/2}$ $cm^{-3/2}$)**	**δ ($MPa^{1/2}$)**
Toluene	8.91	18.3
Xylene	8.85	18.2
Acetone	9.77	19.7
Cyclohexane	8.18	16.8
Methanol	14.28	29.7
Ethanol	12.92	26.2

Table 4: Hildebrand Solubility Parameter for Solvent

Another solubility parameter calculation is developed by Charles Hansen in 1967 explaining on his Hansen solubility parameters. In his theory, he explained on a way to predict if one material would dissolve in another and from a solution. The idea of "like dissolve like" is the fundamental of Charles theory where a molecule is defined as being 'like' another if it bonds to itself in a similar way (Hansen, 1967). In Hansen solubility

parameter, each molecule has three parameters define as δ_d, δ_p, and δ_m, generally measured in MPa

- δ_d The energy from dispersion forces between molecules
- δ_p The energy from dipolar intermolecular force between molecules
- δ_h The energy from hydrogen bonds between molecules.

To correlate between these three parameters, Hansen developed an equation to relate them. According to him, the three parameters are plotted at three-dimensional coordinates, known as Hansen space. He suggested that the closer the value between two molecules, the higher tendency it will dissolve. The correlation is given as below

$$(Ra)^2 = 4(\delta_{d2-}\,\delta_{d1})^2 + \left(\delta_{p2-}\,\delta_{p1}\right)^2 + (\delta_{h2-}\,\delta_{h1})^2 \quad (2)$$

To determine if the parameters of two molecules (usually a solvent and a polymer) are within range a value called interaction radius (R_0) is given to the substance being dissolved.

$$RED = \frac{R_a}{R_o} \quad (3)$$

- RED < 1 the molecules are alike and will dissolve
- RED = 1 the system will partially dissolve
- RED > 1 the system will not dissolve

Substance	δ_d ($MPa^{1/2}$)	δ_p ($MPa^{1/2}$)	δ_h ($MPa^{1/2}$)	R_o
LDPE / HDPE	17.5	4.3	4.1	8.2
PP	17.20	5.60	–0.40	5

Table 5: Hansen Solubility for Polyolefin (Hansen Solubility Handbook)

Substance	δ_d ($MPa^{1/2}$)	δ_p ($MPa^{1/2}$)	δ_h ($MPa^{1/2}$)
Toluene	18	1.4	2
Xylene	17.6	1	3.1
Acetone	15.5	10.4	7.0
Cyclohexane	16.8	0	0.2
Methanol	15.1	12.3	22.3
Ethanol	15.8	8.8	9.4
Naphthalene	19.2	2.0	5.9

Table 6: Hansen Solubility for Solvent (Hansen Solubility Handbook)

2.3 POLYOLEFIN RECYCLING

The disposal of plastic waste is worldwide concern because of its effect on the environment and ecology of the planet. Plastic disposal in landfill sites has become increasingly unpopular because of legislative pressure and public resistance to dumping close to area of habitation (La Mantia, 2002). Plus with the enforcement of waste to landfill must be reduced by 35% over the period from 1995 to 2020, this will give a tremendous effect on the cost for plastic disposal (Achillas et. al, 2007). These pressure, as well as increased environmental awareness and reduced landfill capacity, have led to the development of plastic recycling programs.

Several ways of dealing with plastic waste have been considered – the formulation of biodegradable plastics, thermal recycling, chemical recycling and reuse of plastic waste. There are some incentives for using recycled plastics, including ecological reasons, consumer demand, recycling legislation and lower cost (Tesoro, 1988). After serving their useful life in numerous applications, polymers can be recovered and therefore contribute again to the needs of sustainable development while providing a high level of environmental protection. Various options exist to take further advantage of their properties. While for some materials recycling is the only way of recovery, for polymers there is a full range of recovery options available (Pappa et. al, 2001).

Plastic (polyolefin) can be recycled in many ways: reuse, mechanical recycling, feedstock recycling and energy recovery (Goodship, 2007). Reuse is the common examples of recycling plastic especially on plastic packaging. Unfortunately, reuse is not widely practices because plastic products in general tend to be discarded after first use. Feedstock or known as chemical recycling is a process that includes pyrolysis, glycolysis, alcoholysis and hydrolysis. The aim is to break down the polymer chains into chemical products of lower molecular weight distribution or even in the original intermediates (monomers) which can be used for another complete cycle of polymerization (Paulakis &Papaspyrides, 1996). In other word, this method is to turn back the polymer into its oil hydrocarbon component for use as raw materials for new polymer production (Goodship, 2007). This procedure allows the recovery of more value from plastic waste than incineration, and overcomes some of problems that limit mechanical recycling. However, this process will never probably become a widely used method for recycling large amounts of plastic wastes, but in an integrated approach, it can contribute significantly to solve the problems raised by the disposal of plastic wastes with the recovery of the useful products (Pilati & Toeselli, 2002).

Energy recovery is another method for plastic recycling which is hugely a practice by most countries. Not all plastics can be recycled as their recyclability is influenced by a number of factors such as material composition of the products and amount, cleanliness of the collected waste stream (Plastic Europe, 2014). This method is an effective way to reduce the volume of organic materials. (Achillas et. al, 2007). However, energy recycling has been widely accused as ecologically unacceptable due to the health risk from airborne toxics.

Mechanical recycling also known as physical recycling is the recovery of materials from waste while maintaining the polymers' molecular structure (Plastic Europe, 2014). Mechanical recycling refers to operations that aim to recover plastics waste via mechanical process (grinding, washing, separating, drying, re-granulating and compounding). Mechanical recycling is the preferred route for plastic recycling, simply because it sustains the maximum composition in the plastic waste. In this research, mechanical recycling method is selected. The selected procedure is called dissolution

and reprecipitation method where waste polymer is dissolved in a solvent at a particular temperature. The dissolved waste polymer then is precipitate with anti-solvent to recover the waste polymer back into powder form.

The main aim of this experiment is to find a sustainable solvent that can be developed to dissolve waste polymer (polyolefin) with a high recovery. Studies from previous literature Achilias et. al 2007, conclude that for 1gram of polyolefin polymer, the toluene required is 100g which act as solvent. A very large amount of organic solvent is used but the polyolefin is highly recoverable using this technique. Other research, Pappa et all, 2001 deduced that by using a mixture of 110g xylene and propanol, only 1g of waste polymer can be dissolved. With this situation, it is not preferred to apply in industrial scale as it requires large amount of organic solvent to dissolve the waste polymer. Another setback that is found in previous studies is the dissolution temperature is too high. In Achilias et. al 2007, the dissolution temperature is 130°C, which is higher than the boiling point of toluene. High temperature means it requires more energy if being applied in industrial scale.

In summary, previous research found out a proper way to dissolve the waste polyolefin by using dissolution and precipitation method. However in the studies, the solvent used is not sustainable as a large quantity of solvent needed to dissolve small amount of waste polyolefin and it only dissolves at high temperature. Thus, this research approach is to search a sustainable solvent which can dissolve more waste polyolefin at a lower temperature.

CHAPTER 3 METHODOLOGY

3.1 EXPERIMENTAL FLOWCHART

Experiment methodology in this project is referred to the past experimental procedure that has successfully done. In order to run the dissolution/reprecipitation method for polyolefin recycling, there are 4 main steps that need to follow. The stages are represented as follows:

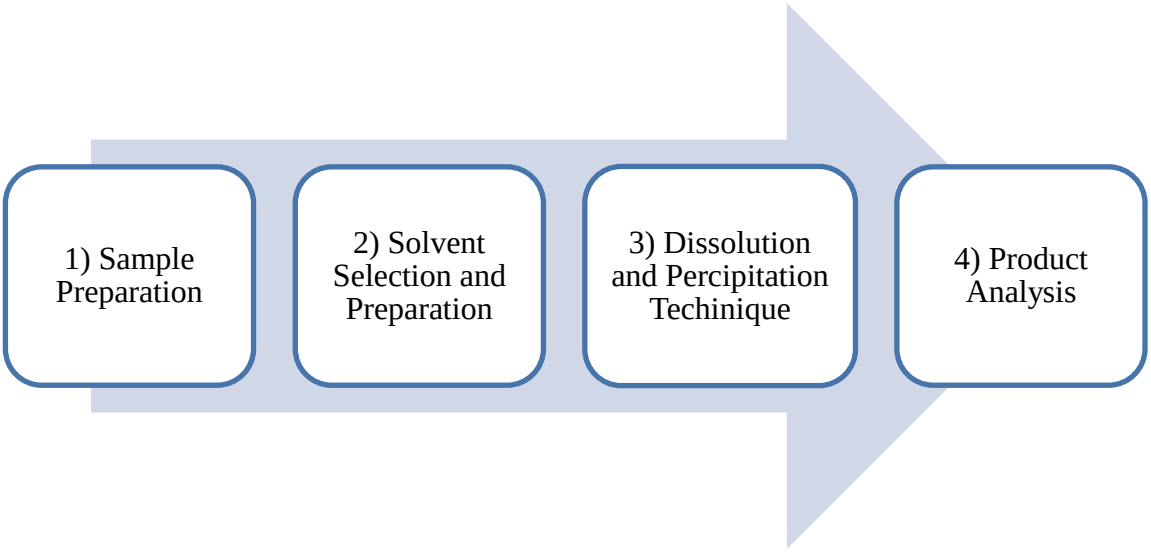


Figure 4: Stages in Experiment Procedure

3.1.1 Step 1: Sample Preparation

In this stage, waste polyolefin is needed to be prepared according to recommended size, which is depending on the thickness of the waste polymer. Recommended size of waste polymer must be 2cm to 4cm (Arkan et. all, 2012). First, the collected waste polymers must be washed with and rinsed with tap water. Then the waste polymer is dried and cleaned before been cut into smaller size.

3.1.2 Step 2: Solvent Selection and Preparation

The next step of this experiment procedure is to select and prepare the solvent. The selection of solvent is based on the right solubility of waste polyolefin. As mention in the literature review, solvent like toluene, acetone, naphthalene is a good combination to dissolve waste polyolefin because of the close value of Hansen solubility parameter.

To prepare a mixture of solvent, first weight the amount of solvent that want to use using a weighting scale. Record the volume for each solvent.

3.1.3 Step 3: Dissolution and Reprecipitation Technique

This stage is the important part of the project, where the recycling of waste polyolefin is taking place. Below is the procedure for dissolution and reprecipitation technique:

1. Heat and stir the solvent in a round flask to a certain temperature (150-180deg C) for 15-30 minutes using a hot plate and magnetic stirrer. This is important to make sure the solvent is ready before dissolution of polymer take place.
2. Weight waste sample of polyolefin dissolve it in the solvent mixture.
3. Insert waste polyolefin little by little and observe the dissolution of polyolefin in the solvent.
4. Wait till the polymer becomes saturated, where it can't dissolve any polyolefin anymore.
5. Cool down the solution till it reaches ambient temperature by stopping the heat from hot plate.
6. Add precipitation anti-solvent into the mixture to reprecipitate the waste polyolefin
7. Pour the solvent into a filter paper and let the waste polyolefin precipitate on the filter paper
8. Dry the recovered polyolefin in oven, weight the final mass and prepare them for further analysis

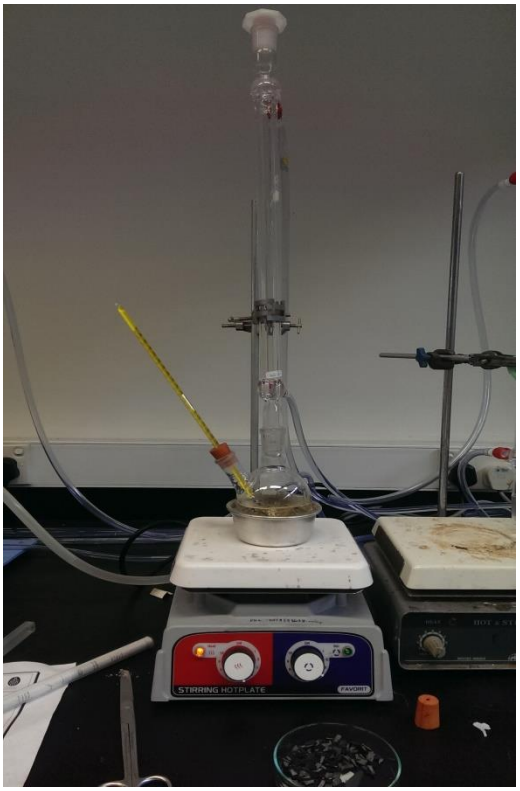


Figure 5: Experimental Setup

3.1.3 Step 4: Product Analysis

After polyolefin are fully dissolved and reprecipitate, then the final recovered product is brought for analysis. This step is to check and examine the purity of the recovered waste polyolefin. This stage will determine the method is recycling polyolefin is successful and economically viable. To examine the properties of the recovered polyolefin, Fourier Transform Infra-Red (FTIR) is used. By using this equipment, the chemical structure of the standard polymers and waste sample plastics before and after recovery can be recorded by examining their IR spectra.

Mechanical structure of the sample is examined to check the tensile stress and elastic modulus for both conditions (before and after recycling). This analysis is important to check on any degradation of recycled waste polymer.

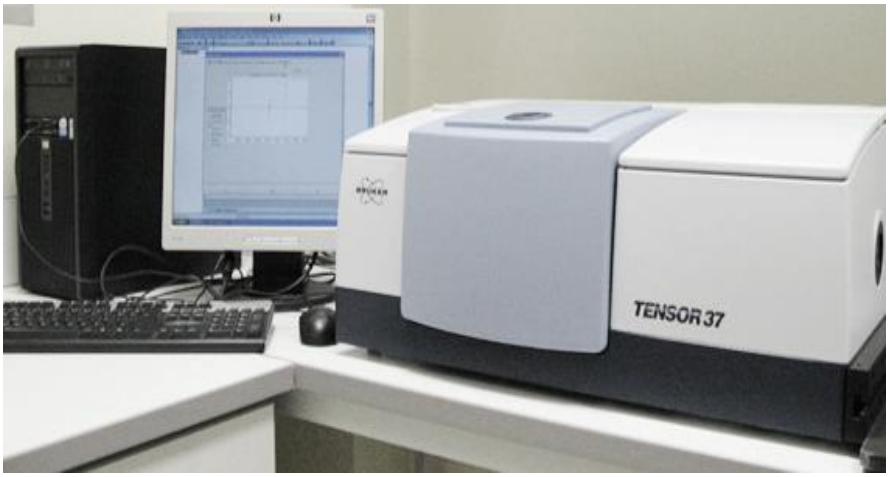


Figure 6: FTIR Equipment

3.2 KEY MILESTONE

Key milestone is a project benchmark to indicate the progress of the project. In this project, the key milestone is identified by the step mention in above methodology. Therefore the key milestone is as below:

Key Milestone	Remarks
Stage 1: Sample Preparation	Completed
Stage 2: Solvent Selection and Preparation	Completed
Stage 3: Dissolution and Reprecipitation Technique	Completed
Stage 4 : Product Analysis	Completed

Table 7: Key Milestone of Project

3.3 PROJECT GANTT CHART

(Refer to Appendix 1)

3.4 EQUIPMENT REQUIRED

Below is the list of tools and apparatus used to complete the project:

No	Objective	Tools Required	Purpose
1	Preparation of Waste Polyolefin	Scissors	To cut the waste polyolefin into smaller pieces
2	Solvent Preparation	Measuring Cylinder	To measure the amount of solvent used
		Weighting scale	
3	Dissolution and Reprecipitation Technique	Magnetic Stirrer and Hot Plate	To heat the solvent and dissolve the waste polyolefin
		Two round neck bottom flask	
		Thermometer	
		Vertical Condenser	
4	Product Analysis	FTIR	To investigate the purity of the recycled polyolefin
		Tensile Stress	To check on mechanical properties

Table 8: List of Tools Required for the Experiment

CHAPTER 4 RESULT AND DISCUSSION

The experiment is conducted using the same ratio of solvent for all three types of polyolefin dissolved at same temperature. For reprecipitation technique, same amount of solvent also been used for all the polymers. Following are the result of experiments that have been conducted in order to see the dissolution take place for all type of waste polyolefin.

4.1 DISSOLUTION OF WASTE POLYMER

The solvent used for dissolution of waste polymer is chosen according to its solubility towards all three waste polymers (LDPE, HDPE, PP). As such, Hansen solubility parameter is being used to determine a good combination of solvent which can dissolve higher amount of waste polymer. From the calculation of Hansen solubility parameter, the Relative Energy Difference (RED) value must be less than 1 in order for dissolution take place. From literature, the value of RED is calculated for all polyolefin on respect to the solvent used (toluene and naphthalene).

Substance	RED	Condition
LDPE / HDPE	0.8	Dissolved
PP	0.98	Dissolved

Table 9: RED calculation from Hansen Solubility Book

4.1.1 Experiment 1: Dissolution of LDPE and HDPE

The first stage dissolution for LDPE and HDPE are done at different percentage of toluene treated with various amount of naphthalene. This is important to find the suitable ratio between toluene and naphthalene do dissolved maximum amount of waste polymer. At this stage, the temperature used is constant at 150°C. The following table shows the amount of toluene and naphthalene used in every trial. From the table below, we can clearly see that the amount ratio of toluene and naphthalene dissolved maximum of 5.13gram LDPE, 5.03gram HDPE is at 90% of toluene and 10% of naphthalene. Once the waste polymer dissolved is maximized, another set of experiment is conducted to determine the possible lowest temperature of dissolution. From the experiment, the lowest temperature of dissolution for LDPE and HDPE are at 90°C.

Toluene (%)	Naphthalene (%)	Amount of LDPE dissolved (g)	Amount of HDPE dissolved (g)	Temperature (^{0}C)
100	0	1	1	150
99	1	2.46	1.68	150
98	2	2.72	1.91	150
97	3	2.94	2.45	150
96	4	3.24	2.64	150
95	5	3.64	2.86	150
94	6	3.87	3.36	150
93	7	4.28	3.72	150
92	8	4.61	4.15	150
91	9	5.04	4.73	150
90	10	5.13	5.03	150
89	11	5.13	5.03	150
88	12	5.13	5.03	150

Table 10: Dissolution for LDPE and HDPE

Solvent	Temperature (^{0}C)	Appearance
90% Toluene, 10% Naphthalene	150	Completely Dissolved
	130	Completely Dissolved
	110	Completely Dissolved
	90	Completely Dissolved
	85	Partially Dissolved
	80	Partially Dissolved

Table 11: Dissolution Temperature for LDPE and HDPE

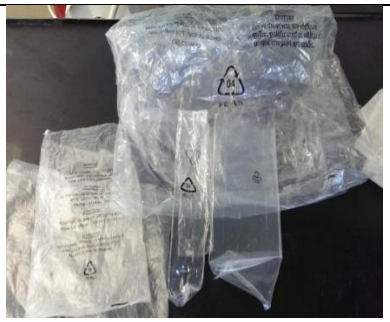
Before dissolution	After Dissolution
	

Figure 7: LDPE before and after recycling

Before dissolution	After Dissolution
	

Figure 8: HDPE before and after recycling

4.1.2 Experiment 2: Dissolution of PP

The same procedure is applied to dissolve PP with constant temperature at 150°C. The following table shows the amount of toluene and naphthalene used in every experiment. From the table below, we can clearly see that the amount ratio of toluene and naphthalene dissolved maximum of 4.13gram PP is at 92% of toluene and 8% of naphthalene. Once the PP dissolved is maximized, another set of experiment is conducted to determine the possible lowest temperature of dissolution. From the experiment, the lowest temperature of dissolution for PP is at 90°C.

Toluene (%)	Naphthalene (%)	Amount of HDPE dissolved (g)	Temperature (^{0}C)
100	0	1	150
99	1	1.5	150
98	2	1.97	150
97	3	2.13	150
96	4	2.76	150
95	5	3.43	150
94	6	3.84	150
93	7	4.02	150
92	8	4.13	150
91	9	4.13	150
90	10	4.13	150

Table 12: Dissolution for PP

Solvent	Temperature (^{0}C)	Appearance
92% Toluene, 8% Naphthalene	150	Completely Dissolved
	130	Completely Dissolved
	110	Completely Dissolved
	90	Completely Dissolved
	85	Partially Dissolved
	80	Partially Dissolved

Table 13: Dissolution Temperature for PP

After the waste polymer is dissolved, then it is precipitated with anti-solvent. In this case the anti-solvent used is methanol. Later the precipitate of the waste polymer is dried and weighted again to calculate the recovery. Following table is the summary of dissolution and precipitation method result.

Before dissolution	After Dissolution
	

Figure 9: PP before and after recycling

Waste Polymer	Polymer dissolved (g)	Temp (^{0}C)	Polymer to Solvent Ratio	Amount of Anti-solvent for Reprecipitation (ml)	Recovery %
LDPE	5.16	90	1:20	Acetone: 13ml	99.5
HDPE	5.03	90	1:20	Acetone: 15ml	98.6
PP	4.31	90	1:21	Acetone: 15ml	99.3

Table 14: Summary for Dissolution and Precipitation Method

From the result of the experiment, it can be observed that amount of waste LDPE dissolved in the solvent is 5.16g at temperature of 90°C. Based on the ratio of solvent and waste polymer, it can be seen that the amount of solvent used is less compared to the studies done by Achillas et. al, 2007, which is 1:100. During the experiment, several temperatures are selected to determine the lowest possible dissolution temperature. It found out that at temperature of 90°C, the waste polymer started to dissolved quickly n the solvent.

For HDPE, it can be observed that amount of waste HDPE dissolved in the solvent is 5.03g at temperature of 90°C. Based on the ratio of solvent and waste polymer, it can be seen that the amount of solvent used is less compared to the studies done before. From the table above, it can be observed that amount of waste PP dissolved in the solvent is 4.31g at temperature of 90°C, which shows significance different form studies done before. For PP, the same dissolution temperature is found which is at 90°C.

4.2 SURFACE CHEMISTRY OF RECYCLED POLYMER

After the polymers wastes are successfully dissolved in the solvent, the precipitate product is being analyzed to check the purity of the component. In this stage it is essential as it will determine whether this solvent of polyolefin recycling technique has reached the outlined objectives or not. FTIR equipment is used to conduct the sample analysis. Following is the graph obtained for the recycled polyolefin.

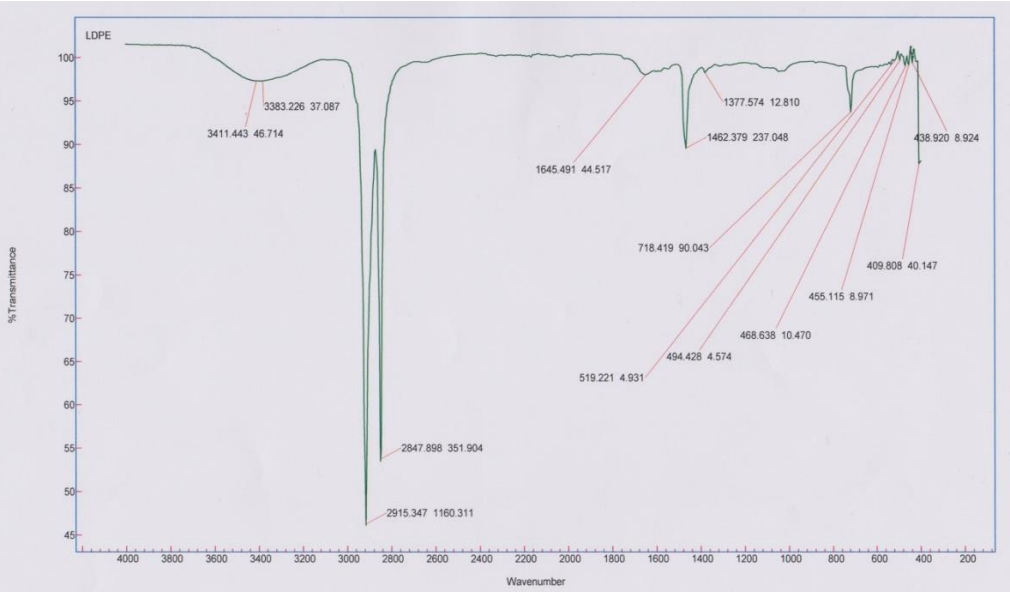


Figure 10: FTIR Graph for LDPE

From the graph X, there is a high peak of transmittance at the Infrared spectrum at wavelength 2800 to 3000, which correspond to the Alkyl C-H stretch. Another peak also can be clearly seen at wavenumber 1460 that indicates CH2 bend. Overall, from the graph obtained in the experiment, it can be deduced that the purity of LDPE is 98% as pure virgin LDPE.

Peak Percentage	Possible Assignment	Strength of frequency
50% at 2915	Alkyl C-H stretch	Strong
55% at 2647	Alkane C-H bond	Strong
90% at 1460	CH2 bend	Strong

Table 15: Summary of FTIR Graph on LDPE

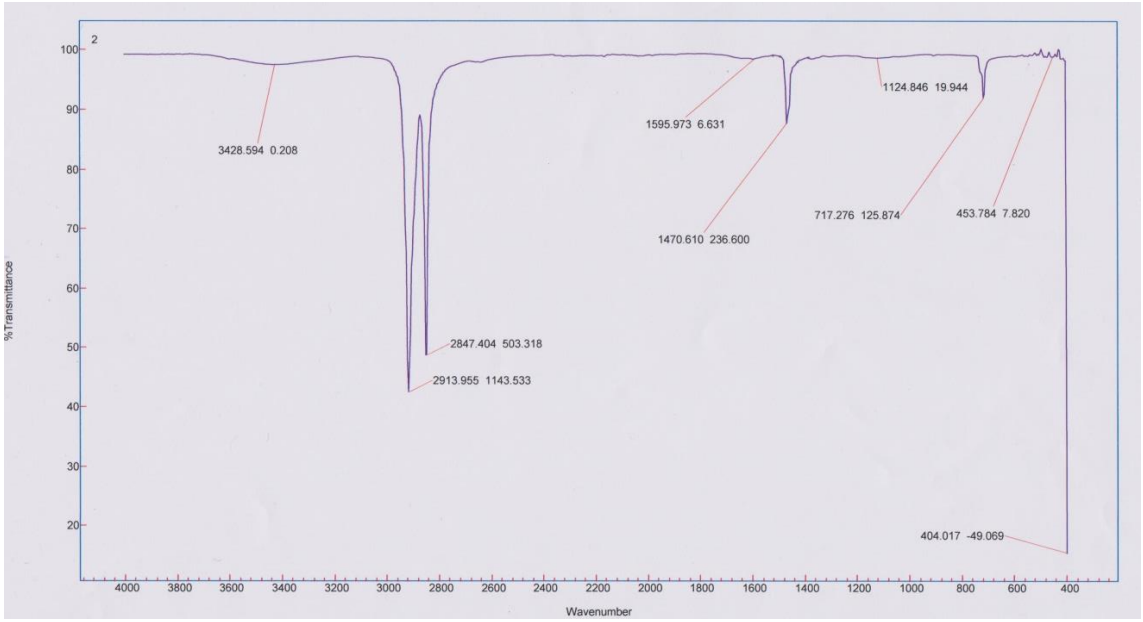


Figure 11: FTIR Graph for HDPE

As for HDPE, the FTIR reading is quite similar to LDPE because of the same chemical components for both polymers. Here the peak is at 2800 to 2900 which clearly shows the Alkyl C-H stretch bond. Secondary peak at 1470 indicates that that there is CH_2 bend in the sample. Overall, from the graph obtained in the experiment, it can be deduced that the purity of HDPE is 98% as pure virgin HDPE.

Peak Percentage	Possible Assignment	Strength of frequency
50% at 2913	Alkyl C-H stretch	Strong
55% at 2847	Alkane C-H bond	Strong
90% at 1470	CH2 bend	Strong

Table 16: Summary of FTIR Graph on HDPE

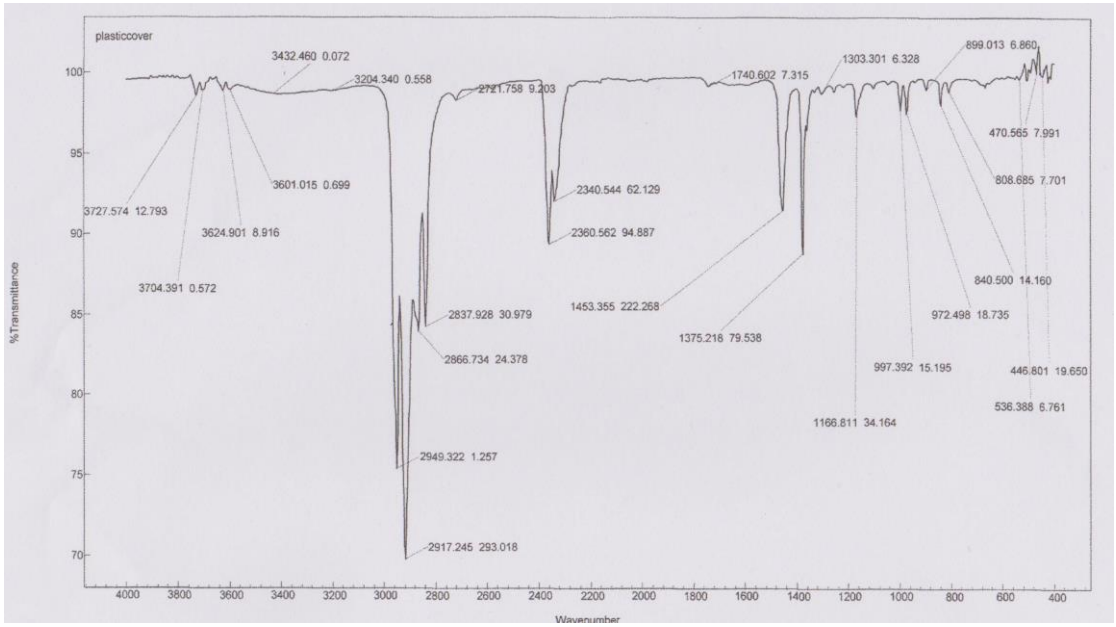


Figure 12: FTIR Graph for PP

As for Polypropylene (PP), the highest peak is 2850-2900 which clearly indicates Alkyl C-H stretch bond. . Secondary peak at 1470 indicates that that there is CH2 bend in the sample. Overall, from the graph obtained in the experiment, it can be deduced that the purity of PP is 98% as pure virgin PP.

Peak Percentage	Possible Assignment	Strength of frequency
50% at 2917	Alkyl C-H stretch	Strong
55% at 2847	Alkane C-H bond	Strong
90% at 1470	CH2 bend	Strong

Table 17: Summary of FTIR Graph on PP

4.3 MECHANICAL PROPERTIES

Tensile mechanical properties are investigated of the waste polyolefin packaging before and after recycling process. Result shows as per below:

Polyolefin		Tensile stress (MPa)	Elastic Modulus (MPa)
LDPE	Before Recycling	14.9	624
	After Recycling	14.7	656
HDPE	Before Recycling	15.6	607
	After Recycling	15.3	664
PP	Before Recycling	20.7	534
	After Recycling	20.4	507

Table 18: Mechanical Properties

From the result in the table above, the data indicates that recycled LDPE and HDPE exhibits tensile stress competent to those of virgin polymer (before recycling). However, there is a clear indication that after recycling the elastic modulus increases. This is possibly due to the influence of fractionation phenomena that happen during the experiment and addictive initially in the original polymer. The same result applied to PP material but elastic modules exhibit slightly lower value after recycling.

In general, we can conclude that there is no degradation of recycled polymer after the dissolution and reprecipitation procedure take place. It can be proven by the chemical and mechanical analysis as per discussion above which maintain the same structure to virgin polymer.

CHAPTER 5 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

After the experiment is conducted, it can be deduced that by using a combination of 90% of toluene and 10% of naphthalene for LDPE and HDPE while 92% of toluene and 8% of naphthalene, more waste polyolefin can be recycled. Following table shows the summary of dissolution of polyolefin according to its type.

Waste Polymer	Polymer dissolved (g)	Temperature (°C)	Polymer to Solvent Ratio	Amount of Anti-solvent for Reprecipitation (ml)
LDPE	5.16	90	1:20	Acetone: 13ml
HDPE	5.03	90	1:20	Acetone: 15ml
PP	4.31	90	1:21	Acetone: 15ml

Table 19: Summary of Experiment result

As stated in the objectives in chapter one, the aim of this experiment is to increase the ratio of waste polyolefin dissolved to the solvent used. From previous study, the amount of waste polyolefin dissolved is at ratio of 1g to 100g of solvent. By doing this combination of solvent, the weight of waste polyolefin finally can be deduced to 1g to 20g of solvent for LDPE and HDPE and 1g to 21g of solvent for PP. Next, our aim is to reduce the dissolution temperature. Previously in literature, the temperature used is ranging from 110°C to 140°C. By using this combination solvent, the temperature of dissolution reduced to 90°C. Having this result indicates a huge milestone to the experiment as the lower the temperature used, the lower the cost of recycling is especially if this method is applied in industrial scale.

5.2 RECOMMENDATION

For the future finding, it is highly recommended to use the same solvent for other type of polymer such as polystyrene (PS), polyvinyl chloride (PVC), or polyethylene terephthalate (PET). Later a trend can be extrapolated to see the behavior and solubility of the solvents toward all types of polymer. Other forward approach from this experiment is to develop other sustainable solvent combination. As we can see there is

several potential solvents can be combined and use as solvent as there is a similarity of solubility parameter with polyolefin such as xylene, cyclo-hexane.

For experimental procedure, there is an inefficiency of the selected equipment used. During the experiment, temperature of reaction is varied up to 180°C. Using the round bottom flask with volatile solvent will keep the pressure inside the flask high. It is advised to use high pressure reactor to keep the pressure low and able to run the experiment smoothly.

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APPENDIX 1

Stage	FYP I														FYP II											
	Weeks																									
Detailed Work	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**
Selection of topic																										
Preliminary Research Review for Literature																										
Preparation for Lab																										
Stage 1: Sample Preparation																										
Stage 2: Solvent Preparation																										
Stage 3: Dissolution Technique																										
Stage 4: Product Analysis																										
Report Writing																										
Presentation and Viva																										

Legend:

Key milestone